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**DEVELOPMENT AND IMPLEMENTATION OF THE
NATIONAL TEST FACILITY (NaTeF) FOR FUELS AND
PROPULSION**

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Purdue University**

**OCTOBER 2013
Final Report**

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14. ABSTRACT The primary goals of this program were to establish advanced practical fuels testing capabilities in the Aviation Technology Department at Purdue University. As the national effort to develop and implement alternative aviation fuels gained momentum, a need existed for additional turbine and piston engine test capabilities, including advanced data collection and exhaust emissions analysis equipment. The project funds were used to purchase an exhaust emissions analysis system for the existing Aviation Technology engine test cells, equipment to study the impact of fuels on aircraft materials, and the development of an engine data acquisition system. The University provided approximately \$158K to support the building renovations and installation effort for the project. With these funds, significant floor space was committed and renovated for the NaTeF effort, including that necessary for the Materials Laboratory and a Piston Engine test cell. Two graduate students are utilizing the turbine engine exhaust emissions capabilities for their research, and results will be published when their work has concluded.						
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1.0 Executive Summary

The goals and mission of the National Test Facility for Fuels and Propulsion (NaTeF) project grew out of past fuels test work during which the need for a controlled environment and advanced testing equipment became clear. The principal investigators of the NaTeF project observed that the effort for alternative aviation fuels at Purdue was missing the capabilities for performance and fit-for-purpose testing at the technological endpoint.

An initiative was then undertaken to identify the essential engine and materials compatibility test equipment, which would be installed in the existing Aviation Technology test cells and a new materials laboratory. The proposal was submitted in the form of a Washington Projects request through the normal channels at Purdue University and was eventually funded by Congress and administered through the Air Force Research Laboratory (AFRL) at Wright-Patterson Air Force Base. Professor David Stanley served as principal investigator, and professors Denver Lopp and Mark Thom were co-principal investigators. Professor Thom led much of the installation effort, while Professor Lopp established important relationships and coordinated collaborative effort for the project.

Although not funded under this project, Professor Davis and Dr. Johnson both supported the project extensively. Professor Davis provided oversight and support for test cell-related activities, while Dr. Johnson supervised PhD and graduate students and led the effort to initiate and establish exhaust emissions research. Matt Johnson, the Aviation Technology Department technician, supervised students and coordinated the work and planning activities with Purdue facilities personnel. NaTeF extends its thanks to Melanie Thom, a consultant hired to develop the Materials Laboratory, for continued service and advice beyond the requirements of her contract.

Project funds were used to purchase the exhaust emissions equipment, develop a data acquisition system, and establish a materials laboratory where the impact of new fuels on aircraft materials could be studied. The University supported the project with funds necessary to renovate laboratory space and establish plumbing, ventilation, electrical service, and physical modifications as necessary to house the new test equipment. The renovation effort necessary for the project led to two project no-cost extensions. The project officially concluded in July 2013, and the capabilities are largely in place, operational, and in use.

Taking into consideration the cost of turbine fuel and the engines available for testing, NaTeF principals made the decision to focus exhaust emissions research efforts for now on smaller turbine engines. Accordingly, the first Aviation Technology PhD student studying in this area developed a plan to study emissions using the Honeywell F109 turbofan engine installed in a NaTeF test cell. This small turbofan produces approximately 1,350 lb of thrust and is similar in size to other engines installed on very light jets and smaller business jets. To date, his work has been limited to Jet-A emissions studies to establish a baseline with the F109 test engine; the

next phase of research will involve test operations with fuels consisting of Jet-A and camelina-based fuel at 25 and 50 percent blend ratios. This research is expected to conclude and all test data should be compiled by March 2014. AFRL supplied all test fuels for this research project.

The NaTeF principals along with other faculty members at Purdue teamed with Mercurius Bio-Fuels in a \$4.6M bio-fuels project funded through the Department of Energy. This initiative is in the first phase during which the fuels development technology is the focus. During the second phase, NaTeF capabilities will be utilized to evaluate the fuel product for performance and specification conformity. In another funded project, test work involving materials exposed to fuel at elevated temperatures was conducted for fuels formulated to replace existing 100 LL aviation gasoline. Piston engine carburetor icing tests have been proposed for funding under the new FAA Center of Excellence for General Aviation (PEGASAS), for which Purdue is the lead university. Additional fuel projects have been proposed and are under consideration for funding or are in contract negotiation at this time. The project created significant opportunities for both graduate and undergraduate study, employment and research.

The final facilities work necessary to support piston engine test is ongoing at the time of this report, and is expected to conclude within a matter of weeks. At that point, the dynamometer and piston engine controls will be extended from the test cell to the control room, and the cell will then be ready for the installation of a piston engine test article.

2.0 Introduction

The need for the development and implementation of the NaTeF became evident to Aviation Technology researchers at Purdue University as a result of previous research and testing of blended turbine fuels conducted during the period 1996 through 1998. That study involved the use of on-wing turbine engines, emissions probes temporarily installed in the exhaust of those engines, and test operations conducted on the ramp of the Purdue University airport. The need for advanced data acquisition and more consistently controlled conditions for exhaust emissions and performance analysis became clear during these tests. Subsequently, the faculty researchers turned their efforts towards improving the existing test cells for research applications, including the acquisition of turbine and piston-based engines.

During this time period, the significance of the fuel issues increased dramatically as a result of both geo-political matters and concerns with greenhouses gases. The United States Air Force and the Department of Defense established goals for the future use of domestically produced bio-fuels. The rationale for these initiatives was largely based on security of fuel sources, whereby new domestic sources would be developed to provide essential liquid fuels for military operations. These efforts moved forward quickly, supported by commercial airlines the interests of which were driven by the need to reduce aircraft CO₂ emissions. From these efforts, two new alternative fuels were approved for blending with conventional jet at 50% by volume [Fischer-Tropsch (FT) fuels from coal and natural gas, and hydroprocessed esters and fatty acids (HEFA) fuels].

The alternative aviation fuels research effort at Purdue University was robust in that the disciplines of mechanical and aeronautical engineering, agriculture, chemistry, and agriculture and biological engineering were all involved at some level. The applications-based capabilities that would enable the testing of new fuels for performance and compatibility, however, were missing or severely limited. Aviation Technology was well-positioned to fill this gap, with existing engine test cells and other important research assets located in the Niswonger Aviation Building at the Purdue University Airport. In 2007, an evaluation of needed, additional capabilities was undertaken by the NaTeF principal investigators – Professors Lopp, Stanley, and Thom - laying the groundwork for the funding request that followed.

The purpose of the project was to develop advanced research and testing capabilities to study the performance of new aviation fuels. Although performance of new fuels could be predicted to a certain extent based on chemical and physical properties, the industry acknowledged that a comprehensive understanding of behavior could only be developed through actual test operations. Fuel consumption, power produced, and exhaust emissions were critically important characteristics requiring full-up engine studies. Materials compatibility was another element that required careful evaluation, as fuels without some minimal aromatic content have led to fuel system and component leak issues.

3.0 Methods

The NaTeF project was largely focused on the development of applications-based fuels research and testing capabilities. To accomplish the goals of the project, the principal investigators needed first to determine which elements were missing or constraining in the overall effort to develop and implement alternative aviation fuels. A review of existing engine test facilities and laboratories equipped to study compatibility issues with new fuels and aircraft materials was undertaken. Special attention was focused on these capabilities located at universities, where faculty members were involved and educational opportunities existed in these application-based areas of research.

After identifying the gaps for research capabilities, the effort then turned to selection of equipment to meet these needs. The principals discussed these topics specifically with the AFRL where scientists and engineers were conducting this type of work. The decision was made to develop capabilities that would complement the AFRL capabilities, enabling NaTeF to support their functions when and where possible. As a result, equipment to support exhaust emissions analysis, data analysis, and materials compatibility testing was given priority initially. For the second phase of the project, equipment to measure engine output power and enable piston engine testing under standard operating conditions was addressed.

4.0 Results

4.1 Facilities and Equipment

The NaTeF project focused on establishing advanced research and development capabilities in two distinct areas: 1) engine test cells, including exhaust emissions, and 2) materials compatibility studies. The current primary focus for the engine test cells is fit-for-purpose testing of aviation fuels, including both new turbine fuels and fuels developed to replace 100LL aviation gasoline. For both of these areas of research, significant facilities upgrades and renovations were necessary, work which was not supported by the NaTeF project funds. The NaTeF principal investigators developed a plan for the facilities and then made a request for support to the University, which subsequently funded this part of the effort at approximately \$158,000.

In order to facilitate engine test research, a number of improvements and adaptations were necessary to existing facilities and equipment, all of which was funded by the University. These included:

- A new fuel system for the test cells
- New horizontal access doors to enable engine installation in the two turbine test cells
- Ventilation, plumbing, and electrical service for the piston engine test cell.

As the project came to a conclusion in July 2013, the university insurance regulations mandated the need for new fuel tanks and some changes to the existing fuel system. Internal funding is available to support these purchases and the work involved; however, the schedule for engine testing and related research will be affected until the work is accomplished.

4.2 Turbine Engine Test Cells

During the first phase of the project, the NaTeF effort was divided largely between the turbine engine test cells and the materials laboratory. The test cells provide the ability to operate and measure the performance of turbine and piston engines with currently used fuels and those under development. Current installed turbine engines include a Honeywell F109 turbofan (Figure 1) with maximum thrust of approximately 1,350 lb, and a Pratt & Whitney Canada PT6-67A turboprop (Figure 2), which produces approximately 1,350 shaft horsepower. The F109 turbofan is a valuable test article for turbine fuel testing given that it has a relatively high bypass ratio of 5:1, is representative of newer turbine engine technology, and consumes modest amounts of fuel. The PT6-67A turboprop engine is a useful engine for test as well in that comparatively little data has been collected on small turboprop exhaust emissions, and this engine is representative of arguably the most ubiquitous line of turboprop engines. NaTeF has access to additional turbine engines, including an Allison 250 turboshaft engine, which is the civilian version of the T63 engine. This particular engine is of significant interest for new fuels testing as it consumes very little fuel in comparison with most jet engines, and may be the most common turboshaft engine in use today.

In these test cells, engine output power, either shaft horsepower or thrust depending on the engine type, can be measured and recorded, along with engine temperatures, pressures, spool RPMs, and fuel consumption rates all of which are important data to determine fit-for-purpose performance of fuels. Both gaseous and particulate matter (PM) emissions can be collected through probes in the exhaust of the test cell engines, and analyzed with equipment described in detail below. As new fuels are developed and brought forward for testing, exhaust emissions are critically important for the final evaluation stages leading to adoption and implementation.

In the test cells, exhaust emissions analyzers, sampling probes, and data acquisition systems were purchased or developed. The exhaust emissions system included an FTIR (Figure 3), a five-gas standard emissions bench (Figure 4), and PM analyzers (Figures 5 and 6). NIST traceable calibration gases were purchased and located immediately adjacent to the test cell control room (Figure 7). Probes for the emissions sampling system were designed and fabricated for both of the turbine engine test cells using ARP 1256 and AIR 6037 as guides for gaseous and particulate emissions, respectively (Figure 8). The gaseous probe is a 3/8-foot stainless steel tube of 0.020-inch wall thickness with a 1/4" stainless shell insert swaged down and welded. The probe is located in the exhaust educator approximately 30" from the exhaust duct of the F109. Following ARP 1256 for guidance, a thermocouple was mounted on a threaded rod and moved vertically and horizontally to determine the boundaries of the high temperature core air in relation to the bypass air and establish the optimal probe location. The probe is not actively cooled as the temperatures for this application are not excessive for the probe materials. Beyond the probe, a 3/8" stainless line approximately 4 feet in length then connects to a filter heated to 160 °C, from which the emissions then travel through a heated line approximately ten feet long to the analyzers. The particulate matter probe has a 1/8" opening after which the emissions enter a 2-inch-diameter chamber where they mix with dry N2 to prevent coagulation. The mixture then enters a 3/8" stainless line and travels approximately four feet before entering a heated line which maintains the temperature of the flow enroute to the analyzers. A flow meter measures the amount of N2 diluting the emissions and a pressure transducer located in the exhaust educator measures the pressure of the exhaust.

The emissions system is installed and operational in the F109 turbofan test cell; the PT6 turboprop test cell is undergoing maintenance and repair, which has prevented emissions test proof operations with that engine. The sampling procedures were developed using ARP 1256 as a reference. Exhaust emissions capabilities will be extended to the piston engine test cell following installation of the first piston engine test article. These systems are described in more detail further down in this report.

Several off-the-shelf data acquisition systems were considered before the decision was made to develop a system specific to the NaTeF testing needs. A post doctorate student was hired to develop the data acquisition system (Figure 9). The system utilizes National Instruments hardware running LabView, samples from 1-1000 HZ, and outputs to an Excel file. It has 64 channels for thermocouples and 32 channels for pressure transducers. The system is fully operational in the control room which is centrally located where it can be extended to all three

engine test cells. The turbofan test cell (Figure 1) is adjacent to the turboprop test cell (Figure 2), and the piston engine test cell (Figure 10) is located in the basement below these two cells. The close proximities of the three test cells make it possible to share the data acquisition and the exhaust emissions analysis systems. New horizontal access doors in view above the engine in Figure 1 below were installed in both the turbofan and turboprop test cells at a cost to the University of approximately \$30K.



Figure 1. Honeywell F-109 Turbofan with Exhaust Emissions Probe, Filter, and Heated Line



Figure 2. PWC PT6-67A Turboprop engine



Figure 3. CAI Model 600 FTIR



Figure 4. CAI Model 600 Portable Emissions Bench



Figure 5. TSI Model 3776 Condensation Particle Counter



Figure 6. TSI Model 3080 Electrostatic Classifier



Figure 7. Calibration Gases



Figure 8. F-109 Turbofan Emissions Probe in Exhaust Duct



Figure 9. Data Acquisition System

4.3 Exhaust Emissions Analyzers

A California Analytics 600-series five-gas portable emissions cart was selected for analyzing gaseous emissions. The system samples at a 1 HZ rate. Gases, ranges, and resolution for this equipment are given in Table 1 below.

Table 1. Portable Emissions Cart Gases

Gas	Concentration	Measurement Range	Resolution	Atmospheric Concentration
CO ₂	%	0 – 20	0.2 %	395 ppm
CO	ppm	0 – 1,000	10 ppm	1 – 15 ppm
O ₂	%	0 - 25	0.2 %	21 %
THC	ppm	0 – 300	3 ppm	0 – 1.5 ppm
NO _x	ppm	0 – 300	3 ppm	0.0001 – 0.100 ppm

This system is used widely to measure exhaust emissions for major gases of interest, including carbon monoxide (CO), oxides of nitrogen (NO_x), carbon dioxide (CO₂), and total hydrocarbons (THC). It consists of three different analyzers – a heated chemiluminescence detector (HCLD), a non-dispersive infrared (NDIR), and a heated flame ionization detector (HFID). The HCLD uses an oven to heat and react nitric oxides (NO_x) with ozone (O₃) to produce nitrogen dioxide (NO₂). The reaction is chemiluminescent, which is detected by a photodiode. The intensity of the light from the reaction is directly related to the concentration of NO_x. The NDIR uses an infrared laser and Raman scattering to detect concentrations of CO from 0 - 1,000 ppm, CO₂ from 0 - 20% and O₂ from 0 - 25%. The HFID measures THC expressed as methane, in concentrations ranging from 0 - 3,000 ppm.

The California Analytics 600 Series Fourier Transform Infra-Red Multi-Gas Analyzer (FTIR) uses the concept of Fourier transform infrared spectroscopy to determine the concentration of gases in a sample of emissions. An internal infrared laser emits light that passes through an emissions sample in varying wavelengths from 1 to 25 µm. Each type of gas absorbs infrared light at slightly different wavelengths. The concentration of gas in the emissions can be calculated by comparing the amount of light received at a detector versus the light emitted. The FTIR can detect the following species at parts per billion to tens of percent per unit volume.

Acetylene	Nitric oxide
Ammonia	Nitrogen dioxide
Carbon dioxide	Perchloroethylene
Carbon monoxide	Phosgene
Chloroform	Propane
Dichlorohylene	Propylene
Ethane	R134A
Ethanol	Sulfur hexaflouride
Ethyl benzene	Sulfur dioxide
Formaldehyde	Vinyl chloride
Methane toluene	Nitrous oxide
Methyl ethyl ketone	

The TSI Scanning Mobility Particle Sizer (SMPS) consists of the Electrostatic Classifier [with a 3085 Differential Mobility Analyzer (DMA)], Condensation Particle Counter (CPC) Model 3776, and a computer. The SMPS can determine the size and concentration of particles in an emissions sample from 2.5 – 3000 nm. The 3080 series electrostatic classifier separates particles from a particle laden sample into different size groups (normally every 10 nm) using a radioactive source and varying voltage source. Once these particles are divided into size bins, they are sent to the CPC for particle counting. The CPC measures the concentration of particles up to 10⁷ particles/cm³. Nanometer size combustion particulates are of growing concern due to their harmful health impacts.

The capabilities of the exhaust emission analyzers are important for the mission of NaTeF, which is largely focused on fit-for-purpose functionality of new fuels. While the fuel chemistry for alternative fuels may appear promising and benign for combustion products, assessment of emissions for different engine types under a wide range of operating conditions is necessary to ensure no detrimental impacts.

4.4 Piston Engine Test Cell

The second phase of the NaTeF project focused on piston engine test cell development. The objective for this cell was to establish piston and turboshaft engine testing capabilities with the primary current focus of supporting the development of new fuels to replace the existing leaded aviation gasoline, 100LL. Three major purchases were made with project funds: 1) a piston engine dynamometer (Figure 10); 2) a conditioned air system which provides intake air to the engine controlled for both temperature and humidity (Figure 11); and 3) cooling system (Figure 12 and 13) for both the dynamometer and the conditioned air system. This equipment enables controlled-conditioned test operations with piston engines, providing standard day conditions or extreme conditions, within certain limitations. Equipment details and specifications are given below.

These capabilities are specifically important at this time when the effort to develop a lead-free fuel to replace 100LL aviation gasoline is moving forward more aggressively. The FAA Center of Excellence for General Aviation lead by Purdue University is expected to conduct research in this area, for which the NaTeF capabilities have been acknowledged as important. Most of the activities for the leaded aviation gasoline replacement effort in recent years have been conducted by FAA Atlantic City Technical Test Center; however, FAA has made it clear that additional test resources are essential in order to carry out the work required under this initiative. The equipment and overall objectives for this test cell were developed in consultation with the FAA to complement their technical test capabilities and be positioned to support the overall research effort in this area.

For this phase of the project, the facilities effort required was significantly higher, as renovations of existing floor space and expansion of services were necessary to meet testing requirements. Although the area had been originally designed and utilized as a component test cell, work to extend plumbing, ventilation, exhaust, and electrical service and install appropriate doors was necessary to adapt it for the specific purposes of this project. Service connections are currently being established between the major pieces of equipment in the piston engine test cell at the time of this report, while doors for the engine test cell remain to be installed.

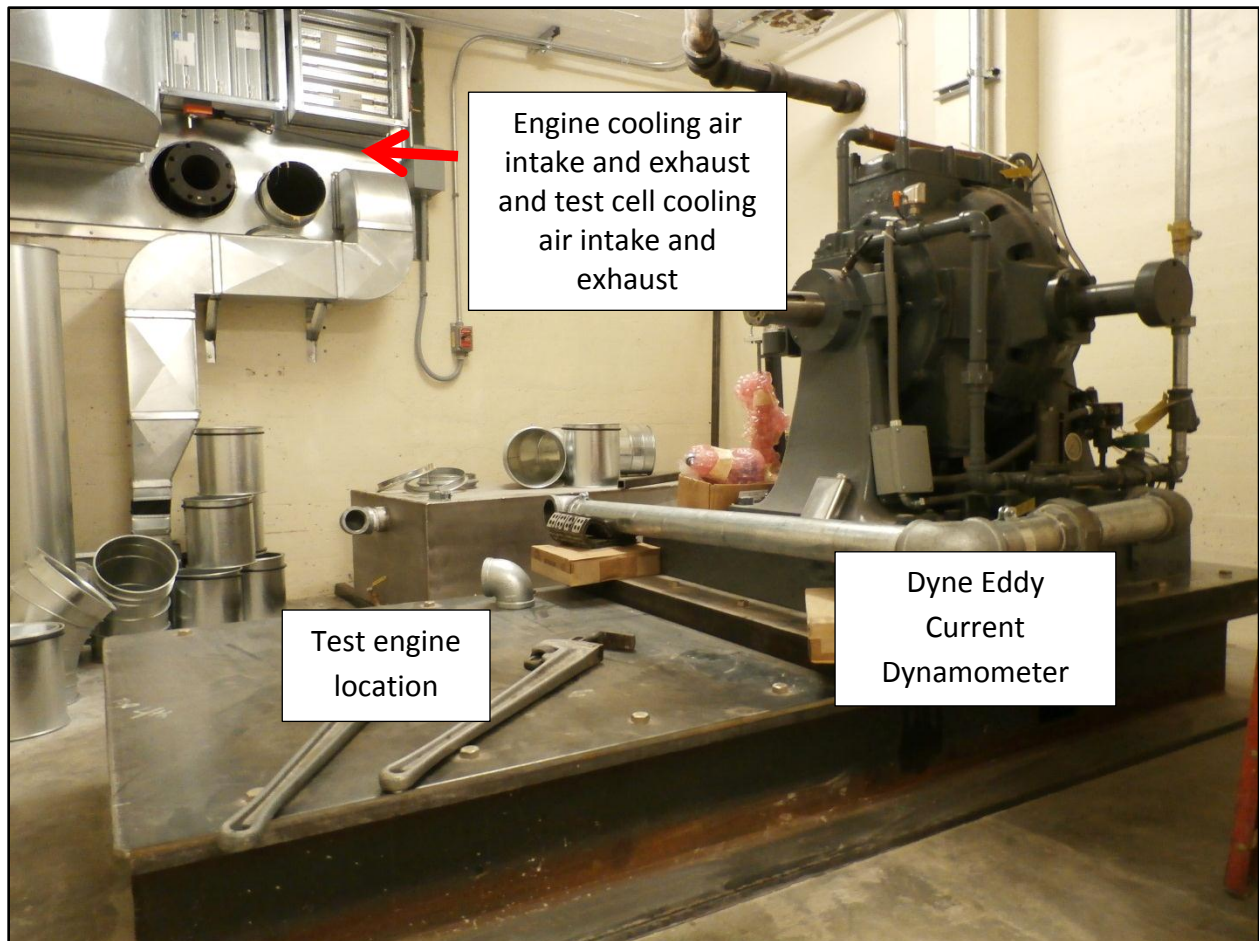


Figure 10. Dyne Piston Engine Dynamometer



Figure 11. ETC model CA5700 Conditioned Air System



Figure 12. Dry Coolers Cooling System



Figure 13. Cooling Tower

The eddy current dynamometer model MW 1519W manufactured by Dyne Dynamometers can accurately measure power from 100 to 500 shaft horsepower in the range of 1200 to 5000 RPM. This range covers a wide number of aircraft piston engines; however, smaller engines of interest for drone applications, and a few large radial engines still in use, fall outside the testing range of this dynamometer. A small water brake dynamometer, not funded through this project, is currently being evaluated for condition and will be renovated as necessary by the manufacturer for NaTeF use in the near future. This dynamometer will have applications for lower horsepower engines, which may be of interest for drone and other military uses, for instance.

Conditioned air will be supplied to the piston engine test article operating on the dynamometer, enabling reliable comparisons of performance under a wide variety of atmospheric conditions. The air conditioning system, model CAS 700 purchased from Environmental Tectonics Corporation (ETC), can provide 700 scfm volumetric flow rate in the dry bulb temperature range of 40 to 120 °F, and 30% to 90% relative humidity. The conditioned air unit, dynamometer, and data acquisition system together enable comprehensive testing of fuels to determine performance under a wide range of atmospheric and load scenarios, including detonation sensitivity, induction icing, horsepower, and specific fuel consumption.

Cooling for the test cell equipment is provided by a system purchased from Dry Coolers. This installation includes equipment, pumps, and controllers adjacent to the piston engine test cell, and a cooling tower with associated equipment located outside the building.

4.5 Materials Laboratory

The overall vision for the Materials Laboratory was to establish a facility for technical support of primarily non-metallic material testing with new fuels. Concerns in the industry over compatibility of fuels with aircraft gaskets, seals, o-rings elastomers drove the need to develop these capabilities for research purposes. Decisions concerning the equipment to purchase for the materials laboratory were made in consultation with Melanie Thom of Baere Aerospace, who was hired to assist in identifying critical needs and capabilities, establish the laboratory, and bring it to operational status. Ms. Thom, a chemist who had been deeply involved in ASTM, CRC, and other fuel-related activities, brought her expertise to NaTeF and continued to provide advice to the principals beyond the conclusion of her contract. The initial effort undertaken was to review the existing analytical capabilities in comparison with research needs, identify gaps, and develop a list of prioritized equipment for NaTeF. The Materials Laboratory now fully functional occupies two separate, dedicated rooms in the Niswonger Aviation Technology Building. The laboratory equipment is described below.

Another objective for the Materials Laboratory was to create an immersive environment for students, where they could develop an understanding of the sustainability and performance issues related to aviation fuel, while also learning new laboratory and testing skills. It is the learning goal of NaTeF that students will develop knowledge and skills with the equipment and test procedures, experiences which will also prepare them to contribute to the overall research effort.

Materials Laboratory Equipment

Instron Universal Tensile System (Figure 14): Used to test the tensile stress and compressive strength of materials. It can perform many standard tensile and compression tests on materials, components, and structures and is important in the evaluation of new fuels for compatibility purposes.

Nicolet Continuum Infrared Microscope (Figure 15): Combines high-performance IR sampling and visible-light microscopy to produce reliable spatially resolved chemical information from samples. This analysis tool provides visual observation of microscopic samples and chemical characterization of most organic and inorganic compounds. The Materials Laboratory utilizes the microscope for surface analysis of aircraft composite structures before and after exposure to aviation fuels.

Nicolet 6700 FTIR (Figure 16): A FTIR spectroscopy instrument which operation relies on the fact that molecules absorb specific infrared energy characteristic of their structure. This instrument is used to analyze the chemical compositions of solids, liquids, and gases. The Materials Laboratory utilizes the spectrometer in analysis of the aircraft components as well as aviation fuels.

TA Instruments Q50 TGA (Figure 17): Utilizes thermogravimetric analysis to measure the amount and rate of change in weight of a material as a function of temperature or time in a controlled atmosphere. It is widely used in both research and quality control laboratories. TGA is particularly useful for measuring thermal stability, decomposition kinetics, composition, estimated lifetime, oxidative stability, and moisture and volatile contents. The Materials Laboratory uses the Q50 TGA to examine the effect of fuels on aircraft parts, especially on elastomers.

HP 5980 Gas Chromatograph (GC) (Figure 18). GC is used to separate, identify, and quantify chemicals in a complex sample, an important capability for fuels testing and characterization.

Parr 4830 Bomb Calorimeter (Figure 19): A constant-volume calorimeter used to measure the heat of combustion of a reaction, which provides the information required to calculate the heat of combustion specific to the fuel under test. This is one of the most important characteristics of any fuel, relating specifically to the range achievable by the aircraft.

Petrotest PM-4 Flashpoint Tester (Figure 20): Identifies the flash point of a volatile material, which is the lowest temperature at which it can vaporize to form an ignitable mixture in air. This is a critical parameter for determining the safety of fuel storage and utilization, and is one which must be understood for new fuels under consideration.

Vented hood (Figure 21): Removes vapors and odors during testing.

Fisher Tensiomat 21 Surface Tension Tester (Figure 22). This equipment is used to measure the apparent surface tension and interfacial tension of liquids, an important characteristic of fuels.

Mark Balance with Density Kit (Figure 23): Enables measurement of the density of both liquids and solids. Density of fuels is a critical characteristic.

Shore Durometer: Enables measurement of the hardness of a material. Hardness may be defined as a material's resistance to permanent indentation. This equipment is used in the Materials Laboratory to determine hardness in polymers, elastomers, and rubbers, characteristics which may be altered by fuels.

Spectronic Ultraviolet–Visible Spectrometer. Provides details on specific chemical structures of the samples, information which is important in the evaluation new fuels.

Oven: Provides elevated temperature environment to study the interaction of fuels and materials.

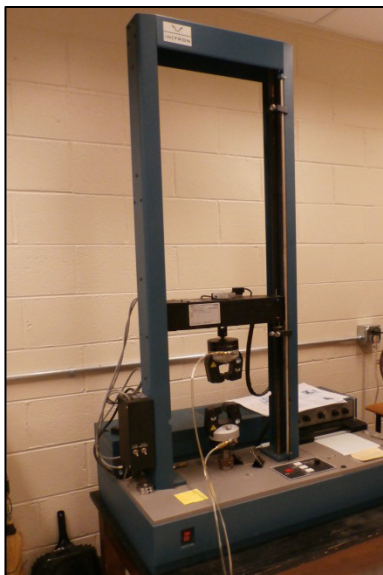


Figure 14. Instron Universal Tensile System



Figure 15. Nicolet Continuum FTIR Microscope



Figure 16. Nicolet 6700 FTIR

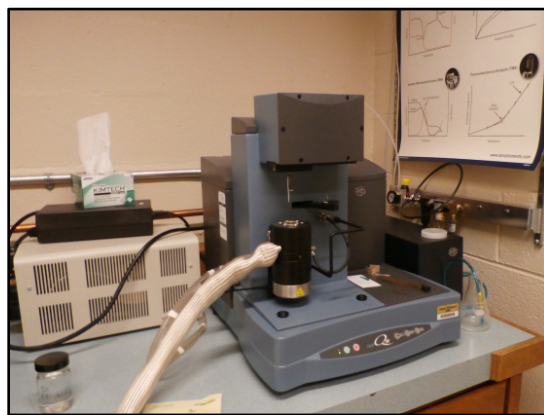


Figure 17. TA Instruments Q50 TGA



Figure 18. HP 5980 Gas Chromatograph



Figure 19. Parr 4830 Bomb Calorimeter

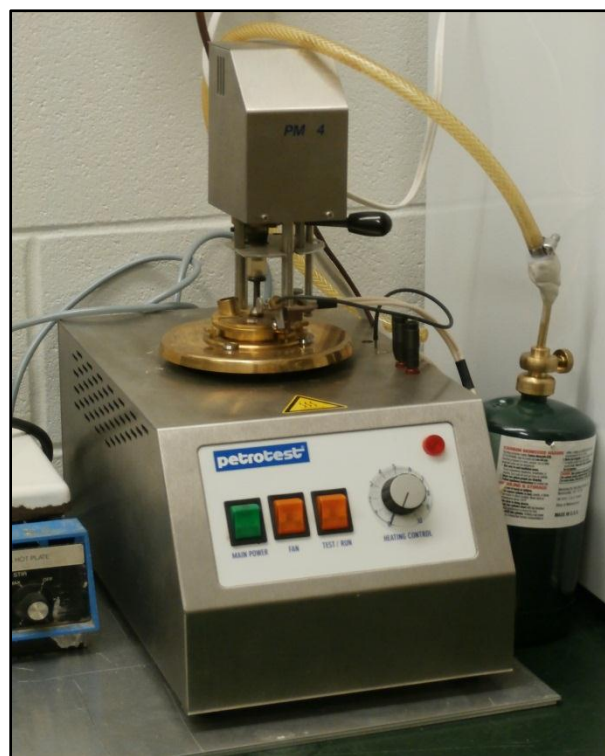


Figure 20. Petrotest PM-4 Flashpoint Tester



Figure 21. Vented hood



Figure 22. Fisher Tensiomat 21 Surface Tension Tester

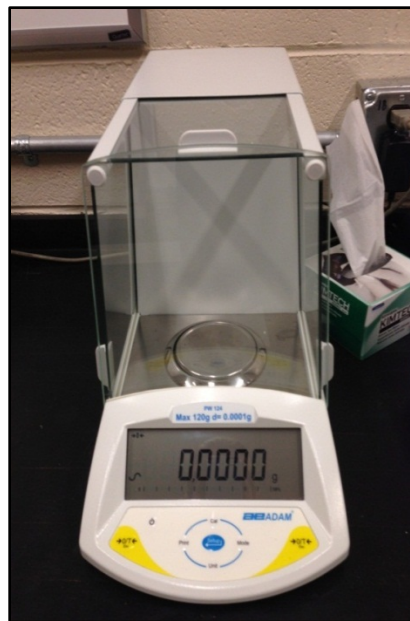


Figure 23. Mark Balance with Density Kit

5.0 NaTeF Research Activities

The NaTeF Materials Laboratory capabilities have been used to conduct research for both piston engine and turbine engine applications. Work to date described below has included internally funded research for graduate studies, and sponsored research. The opportunities for fuels and related research activities are expected to increase significantly as a result of Purdue's role and participation in two newly-awarded FAA Centers of Excellence (COE) – the COE for Alternative Jet Fuels and Environment and the COE for General Aviation (PEGASAS). The NaTeF facilities and overall capabilities were identified as key elements for both the original COE proposals submitted to the FAA.

Turbine engine emissions studies have been performed with funding provided by the Aviation Technology Department and fuel supplied by the Air Force Research Laboratory. Studies of research literature led to the conclusion that more emission testing had been performed with larger turbine engines and less emissions data was available for small turbine engines. The ICAO engine databank, for instance, reflected exhaust emissions data for engines of greater than 6,000 lb maximum thrust and the AAFEX and AAFEX 2 studies were conducted with large turbofan engines. Accordingly, the first Aviation Technology PhD student conducting research in this area developed a plan to study gaseous emissions using the Honeywell F109 turbofan engine installed in a NaTeF test cell. This small turbofan was considered ideal in that it consumed very modest amounts of fuel and was similar in size and performance to other engines installed on very light jets and smaller business jets. For graduate research conducted without external funding, this exhaust emissions project was deemed both valuable and supportable. To date, this work has been limited to Jet-A emissions studies to establish a baseline with the F109 test engine; the next phase of research will involve test operations with Jet-A and camelina-based HEFA fuel at 25% and 50% blend ratios. This research is expected to conclude and all test data should be compiled by March, 2014. AFRL supplied all test fuels for this research project.

A funded research project studied the effect of a new fuel formulated to replace 100LL aviation gasoline on aircraft materials listed under ASTM D7826. This research project, utilizing equipment and capabilities in the NaTeF Materials Laboratory, was recently completed and findings submitted to the sponsor.

This year, Purdue teamed with Mercurius Biofuels, a Washington state energy company, for a \$4.6M Department of Energy project studying the conversion of corn stover to jet fuel. The NaTeF capabilities to characterize fuel and conduct engine testing and materials compatibility studies were identified as key strengths in the original proposal. In the second phase of this project, NaTeF will perform fit-for-purpose tests with the new fuel developed under Mercurius technology.

Utilizing the Nicolet 6700 FT-IR instrumentation in the Materials Laboratory, Melanie Thom, a chemist sub-contracted under the NaTeF project, completed the study entitled "TGA-FTIR

analysis of polymers, investigation of methodology for understanding polymer/fuel exposure responses and interactions". A draft of the report is included in the appendix.

In each of the laboratories and test cells of NaTeF, procedures to operate equipment and to conduct test operations have been developed. While much of this information originated in vendor manuals and publications, the combination of equipment and complexity of the systems operating together made it necessary to develop operational and procedural steps from the fundamental level forward. Test procedures, on the other hand, continue to evolve in response to specific requirements.

Over the past year, the AFRL has provided NaTeF with significant quantities of fuels for testing purposes, including that necessary to power the Phenom 100 Jet on a demonstration flight of bio-fuels to the Oshkosh Air Show in early August 2013. These samples of test fuel have made it possible for two Aviation Technology students to investigate emissions in small turbine engines as part of their graduate studies. Without the support of the AFRL, these projects and research efforts would not have been possible. The NaTeF principals would like to extend their thanks and appreciation to the USAF and the AFRL at Wright Patterson Air Force Base for their support.

6.0 Challenges Encountered

The NaTeF project involved a number of challenges for facilities and personnel. Renovation of existing space led to unexpected changes and considerable time spent in planning and modifications. While the original building had significant floor space dedicated to testing, including areas designed for fuels and high speed machinery research, the upgrades necessary for electrical power, air, and plumbing were substantial both in terms of costs and time. Insurance requirements understandably drove the need for significant changes throughout the project, as well. The single most challenging issue during the project was establishing the piston engine test facility in the basement of the building. This location was weighed against other options in the building and in other nearby facilities, and the decision was finalized only after thorough consultation with Purdue Facilities and Fire and Safety personnel.

Personnel issues arose as individuals working on the NaTeF project developed knowledge of systems, equipment, and project planning, and then moved on to other projects or to jobs following graduation. Even though a system of thorough recordkeeping for equipment operation, procedures, and processes was established, no amount of forethought and planning was sufficient to prevent some loss of experience and knowledge as a result of the normal turnover that occurred during the course of the project. These issues were most noticeable during the summer months when the assigned work crew was at the lowest number. As the project concluded, thought was paid to the processes necessary to maintain the working knowledge necessary to operate and support the equipment and facilities.

A few original project objectives were not completed by the project end date. The effort to design and fabricate a seal test rig to evaluate the impact of new aviation fuels on sealing function has not been completed. Some design and personnel issues encumbered this effort, although the steps taken were certainly instructive and pointed towards a practical solution. The principal investigators have determined a path forward using fuel system components, an effort which will most likely require the support of component manufacturers, given the cost of the equipment. In the piston engine test cell, the first test engine remains to be installed, a step which is necessary to conduct proof operations for the dynamometer and conditioned air supply system.

7.0 Future Plans for Additional Resources and Capabilities

As the NaTeF project moved forward, additional equipment and resources that would be important for the future were identified. These include:

- Additional tenure-track faculty members whose research interests will be served by NaTeF. Currently, a chemical engineering post doctorate funded by the Provost is assisting NaTeF and the AirTIES Research Center in the new fuels research effort. This individual will assume a Visiting Professor position in the Aviation Technology Department in the Spring 2014 semester. Under this one-semester appointment, she will teach a graduate course in aviation fuels and conduct fuels research under the AirTIES Research Center. The next step will be to pursue a Strategic Hire with the objective of hiring her into a tenure-track faculty line position.
- Full-time technical support for NaTeF and related research facilities under Aviation Technology.
- Altitude simulation equipment for piston engines. Such a system coupled with the ETC conditioned air system will facilitate high level testing and research for future piston engines and fuels.
- Additional exhaust emissions equipment, including specific PM emissions analyzers to be determined. As bio-fuels are developed, exhaust emissions, including specifically PM emissions, will be a significant hurdle to cross on the path to full adoption.
- A comprehensive fuels laboratory, a resource which does not currently exist at Purdue. The NaTeF Materials Laboratory is equipped to perform a significant level of fuel testing; however, as it stands now, some work to fully characterize fuel must be done in other facilities. Having all these capabilities in one facility at Purdue University will be beneficial both for the NaTeF project and for other disciplines involved in fuels research.
- Elevated temperature wet fuel rig to study the impact of high temperatures on fuel system components. An effort to establish these capabilities in collaboration with an aerospace company is underway at this time.

8.0 Future Research

Purdue University is the lead institution in the FAA Center of Excellence (COE) for General Aviation. NaTeF was identified as a critically important resource during the COE selection process. The FAA will fund the effort to develop replacements for 100LL (leaded) aviation gasoline through this Center. Purdue, again with NaTeF and AirTIES playing prominent roles, is a core institution in the FAA Center of Excellence for Alternative Jet Fuels and the Environment, the Center through which funds for new aviation fuels will be channeled. These two Center initiatives have just been launched, and the research initiatives will take some time to unfold under FAA guidance. Nonetheless, the challenges and some of the specific testing required for the fuels research effort are known, and are included in the list below of future research projects and studies.

- Carburetor icing tests with candidate fuels under development to replace 100LL aviation gasoline. Studies of this nature require control of intake air characteristics for both temperature and humidity, capabilities that NaTeF equipment can provide.
- Detonation testing and performance evaluation of unleaded replacement fuels for 100LL aviation gasoline.
- Exhaust emissions analysis of small turboprop engines with both Jet-A and new turbine fuels. The concern over carbon emissions will continue to drive research in these areas, where less work has been done with smaller engines.
- Material compatibility studies with new fuels. New fuels will continue under development, and it is expected that no single new fuel will solve all of the issues. As a consequence, the ability to conduct testing for materials compatibility and general performance of fuels will be important into the foreseeable future.
- Component performance and durability studies with new fuels and fuels at both elevated and low temperatures.
- Development of streamlined testing processes that will enable more cost effective and rapid approval of new fuels. This initiative would require collaboration on the part of a number of stakeholders, including ASTM.

9.0 Conclusions

The NaTeF project was unique in that the objectives were to establish expanded and advanced practical fuels testing and research capabilities in a university setting. The challenges were significant, and not all of the goals have been completely fulfilled at this point, although these consist primarily of installation details nearing completion. In parallel with the NaTeF effort, the principals also established a new research center, “The Air Transport Institute for Environmental Sustainability” (AirTIES), at Purdue University. The mission of this Center is to bring together under a collaborative umbrella the research elements needed to develop, test, and fully implement new aviation fuels. Two aerospace companies have joined the Center as industrial partners, and nearly 40 faculty members from the broad disciplines of engineering, agriculture, and science have participated with AirTIES, as well. NaTeF represents a wide range of testing and research capabilities that are critically important to the mission of the AirTIES Research Center.

An additional goal of AirTIES is to establish a curriculum for “Sustainable Aviation and Transportation Operations” which brings significant focus to the topics of alternative fuels, carbon emissions, and related topics. This new Area of Concentration (AOC) as proposed is comprised of four new graduate level courses, including one focused on aviation fuels and emissions, and another on topics of sustainability for aviation. Approval of this AOC is expected during the fall semester, 2013. The curriculum effort closely supports the goal of NaTeF to develop learning opportunities for students interested in aviation fuels and the overall topics of environmental and economic sustainability. The engine test cells and materials laboratory enable students to gain hands-on experience in a true testing environment where they will develop new skills, knowledge, and awareness important for their future careers. Student interest is apparent, and faculty expectations are that enrollment, including students from other disciplines, will grow over time.

The College of Technology, the home college of the Aviation Technology program, committed the services of Dr. Gozdem Kilaz, a post doctorate researcher in bio-fuels, to AirTIES for the fall semester, 2013, with a plan to bring her into a faculty position to support the mission of the Center in the following year. This represents a significant and timely commitment to the aviation fuels research and education efforts of AirTIES and Aviation Technology. The College also funded the ½-time appointment of a PhD student, Richard Simmons, over the past year. Over this time he has supported NaTeF in the solution of technical problems and project development; his appointment will continue for the academic year 2013 – 2014, during which he is expected to take a lead role in project management and research proposal preparation.

10.0 Recommendations

The NaTeF project has established a unique and powerful combination of capabilities that enable evaluation of fuel performance and fit-for-purpose at the technological endpoint. Moving forward, it is important that NaTeF partner with other testing organizations and facilities to leverage combined capabilities for advanced fuels research. NaTeF researchers should pursue opportunities for study and collaboration with other institutions and with AFRL when and where possible. It is the hope of the principals that collaborative research and engagement opportunities may develop with AFRL, as the testing capabilities come into full use and operation.

Through this project, the foundation has been laid to support advanced learning in powerplant and fuel testing and research for both undergraduate and graduate students at Purdue. The test cells and Materials Laboratory facilities enable students to immerse themselves in a testing and research environment where cutting edge research is underway. Opportunities for advanced student learning should take first priority, as thought is given to future projects and initiatives.

NaTeF and Aviation Technology together with Cirrus and Continental Engines should pursue the development of a green flight training fleet at Purdue, eliminating a significant source of lead for piston engine operations and reducing the carbon footprint of the turbine engine aircraft, as well. Committing to these types of goals make sense for an organization dedicating significant resources to fuels and exhaust emissions research. Creating opportunities for students to participate in such an effort sets the appropriate tone for social responsibility while also establishing a living environment where advanced, practical learning may occur.

Appendix

TGA – FTIR Analysis of Polymers

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TGA – FTIR Analysis of Polymers

Investigation of Methodology for Understanding Polymer/Fuel Exposure Responses and Interactions

Background

One of the ongoing challenges for fuel designers is the question of an aromatic content requirement for alternative fuels. It is generally accepted that the presence of “aromatics” is necessary to attain expected polymer swell to provide protection against leakage. The challenge is to define what aromatic should be added and how much. From a performance standpoint, aromatics are an undesirable component, particularly from an emissions and energy content perspective. Ideally, as with any additive, as little as possible should be added to provide the desired outcome. The challenge is in defining the desired outcome beyond “swell”.

The current method used for determining swell relies on traditional static exposure tests. Samples are placed in a beaker of test fluid and the amount of swell (volume), density, and hardness change is measured. It is understood that this methodology has limitations and due to both the static nature of the exposure and the lack of realistic seal containment. Researchers are studying methods to improve this exposure (Graham, UDRI; Stanley, Purdue).

While research has been done successfully to assess the amount of impact various aromatic classes have on swell (Graham), currently, no reliable analytical method exists to screen quickly potential aromatic additives for their impact on the polymer structure. If a researcher had a clear set of analytical behavior to mimic, then aromatics could be added and evaluated. Currently we do not have a quick analytical answer of how is the aromatic interacting with the polymer, i.e. is it substituting for components in the polymer, is it adding to the components, or is it breaking polymer chain bonds? Once we know “what” it is doing, then we have the opportunity to pursue adding aromatics such that it “keeps doing the same thing.”

Research to date has developed a very comprehensive list of aromatics present in traditional jet fuel. Obviously the answer is not to add all of them. However, we can select aromatic materials from that list and feel confident we are not adding something “new”. We can also select an aromatic and evaluate its behavior on a macro-scale, i.e. what is the percentage of swell in a soak test or the change in tensile. That is only half the story. Previous fuel switch incidents indicate the fuel/polymer interaction is more than just the physical swelling, it also the breakdown or change to the polymer in the working environment.

Current analytical technology permits the coupling of Thermogravimetric Analysis (TGA) with Fourier Transform mid-infrared analysis (FT-IR). The concept is that the TGA analysis tells you when various thermal events happen, i.e. the evolution of an absorbed chemical, how fast it happens and how much is evolved (weight percentage). The FT-IR can then be used to identify the evolved gas. By coupling the two methods, it is theoretically possible to assess what changes have taken place in the polymer post exposure: How much material is there that was not before, when does the polymer thermally breakdown and is it different, or are there new chemical species that were not there before?

The individual methods are not new. The challenge is to develop the hyphenated methodology, to determine if the assessment provides valid data, and to correlate the results to observed physical behavior. Once a method is validated, it can then be used by fuel developers to select aromatics and concentrations that will provide similar fuel/polymer interactions.

Installation

The Nicolet 6700 was received 18 February 2010 but installation was delayed by the lack of available shop air. The installation was halted on 12 March 2010 and did not resume until May 2010. Final installation of the FT-IR was completed in May 2010. Work on the TGA-FTIR effort was further delayed by the loss of an existing heated gas cell, requiring the purchase of a replacement. A purge air generator was overlooked during the ordering process and was ordered after the installation of the FT-IR.

The TGA purchase was made with Phase II funding. The TGA was received 30 December 2010 and was installed January 2011. The heated gas cell arrived July 2011.

The building air experienced excessive water in the lines due to a part failure in the building compressor in January 2011 and was taken off-line. The compressor was repaired January 2012.

Because of water exposure due to the compressor failure, a valve was corroded and resulted in a part failure in the TGA. In order to protect the TGA, a protective water separator/filter assembly was added to the TGA air line.

The actual TGA-FTIR research project began 28 September 2012.

Installation Challenges

Challenge	Resultant delay
Access to clean shop air	6 months
Procurement of Purge generator	3 months
Installation of Purge generator	6 months
Procurement of heated gas cell	9 (including funding delay)
Access to TGA training	Never received
Procurement of cured polymer slab stock	3 months
Second shop air failure	12 months

Other Projects Using Facilities

One of the NaTeF goals was to make use of the installed laboratory equipment in support of other projects. Within the grant period the facility was used by both internal and external departments in support of class and research activities. Projects included:

Activity	Source	Task
IR	Internal	Identification of contamination in the departments B727
Lab work	External	Support Chemistry student research
IR	Internal	Second B727 contamination investigation
IR	Internal	F109 test engine contaminant investigation
IR/Lab	Internal	Approval of Honeywell Jet Fuel Blend for use in B727
IR/Lab	External	Swift compatibility study

Literature Review

Two separate literature review activities were undertaken. The first was to understand the research regarding the impact of a variety of aromatic classes and families had on polymers. This research was focused on the work of Dr. John Graham of UDRI and provided insight on what were the impacts on volume changes of the different aromatics. It was noted that the focus of this work was to monitor how much each chemical impacted the volume change characteristics of the polymers, as opposed to the mechanism of the polymer interaction with the fluid. Articles reviewed included (Graham, Striebich, Minus, & Harrison III, 2007), (Dewitt, 2008),

Based on the research (Graham, Striebich, Minus, & Harrison III, 2007), it was confirmed the polymer most impacted by exposure to synthetic fuels was the nitrile rubber, one of the materials selected for this research. Further research found a relationship between solubility parameters and with respect to the polarity. As the polarity increased in a given family of aromatics, so did the volume swell. Similarly, as the molecular weight decreased, the volume swell increased. Therefore, it is indicated that the greatest swell in nitrile rubber will be by highly paraffinic synthetic hydrocarbon fuel due to the small aromatic molecules with significant polar character (Graham, Striebich, Myers, Minus, & Harrison III, 2006). Nitriles with higher plasticizer contents will be more impacted by the exposure than those with lower plasticizer content (Graham, Striebich, Minus, & Harrison III, A Rapid Survey of the Compatibility of Selected Seal Materials with Conventional and Semi-Synthetic JP-8, 2007).

In fluorocarbons, it was confirmed that fluorocarbons experience little fuel swell so there was no relationship between the swell of fluorocarbon and aromatics (Graham, Striebich, Minus, & Harrison III, The Swelling of Selected O-Ring Materials in Jet Propulsion and Fischer-Tropsch Fuels, 2004).

A second literature review was done to better understand the methodology of using TGA and FT-IR to analyze samples, particularly polymers (Garavaglia, 2013) (JASCO, 2005) (Maciejewski, Eigenmann, & Baiker, 2001) (Manley, 1989) (Netzsch) (Perkin Elmer) (Singh, Wu, & Williams, 2012), (Liu, Wilson, & Theato, 2011).

Based on this analysis it was determined that there were four ways that polymers will thermally degrade – depolymerization, chain scission, side group elimination, and actual oxidation. Depolymerization is characterized by the monomer building block, aka the repeating unit along the backbone, being cleaved off the end of the chain, one block at a time. Chain scission occurs when the polymer backbone is randomly broken. The third way, side group elimination is described as pendant groups that are not part of the main backbone are lost. This occurs due to a weaker bond strength of the pendant group to the backbone. The fourth, oxidation, occurs when the polymer chain is actually oxidized, resulting in the formation of CO, CO₂ and H₂O (xxx citation). Oxidation of the polymer can be seen by the FTIR as spectra displaying peaks at 1400 to 1300 cm⁻¹ (CO), 2300 – 2000 cm⁻¹ and 750-500 cm⁻¹ (CO₂), and 3700 – 3500 cm⁻¹ (H₂O) (Maciejewski, Eigenmann, & Baiker, 2001), (Singh, Wu, & Williams, 2012). Singh, et.al. also reported on the observation of a doublet peak at 2250 to 2000 cm⁻¹ which they determined was the result of CO. The spectral peaks were observed from TGA gases evolved at room temperature and 400°C and were attributed to dehydration. Based on these degradation methods, it may be possible to see the impact of the fluid exposure as a change in the degradation method.

In addition to reviewing findings, the available literature was also scanned for information on the experimental set up used to develop the results. Based on this analysis, typical experimental set ups included: 25°C/min to 110°C in a nitrogen environment followed by a 10 min hold, then 25°C/min to 900°C with another 10 minute hold (Singh, Wu, & Williams, 2012) and running 20°C/min from 20°C to 850°C in nitrogen (Garavaglia, 2013). Recommendations from TA Instruments suggest that a 5°C or 10°C/min ramp is sufficient for most TGA-FTIR analyses, the slower ramp providing greater separation of the evolved gases but possibly diluting the gases to the point the FTIR cannot register spectra.

Polymer Study

The study to date has been comprised of two simultaneous activities; the learning curve related to the equipment itself and the research to develop a test methodology and determine if the method can provide information regarding the molecular interactions between the polymers and test fluids. To develop the methodology, testing began with unexposed polymers exposed to a variety of experimental conditions, exposed polymers with increasing length of fluid exposure, and analysis of baseline exposure fluids.

Timeline

- 28 Sept 2011 Initial testing began using provided polymer materials that had not been exposed to any fuel. This was also the initiation of the learning curve for the use of the TGA equipment due to an inability to coordinate and procure supplier training.
- 27 Jan 2012 Oxidizing gas becomes available
- 28 Mar 2012 First fuel exposed tests
- 10 May 2012 Begin understanding the spectral analysis and interpretation, especially with respect to oxidation of the parts
- 17 May 2012 Introduce Aromatic 150 as a soaking fluid

May – June 2012 Procure multiple experimental runs but limited data interpretation. Effort focused on methodology and execution

July – Sept 2012 Testing suspended due to other NaTeF obligations

11 Oct 2012 Supplier technical assistance requested to understand better the test methodology and data interpretation

Oct 2012 Literature research on methodology

24 Oct 2012 Introduce S-8 synthetic jet fuel as a soaking fluid

Oct 2012 – Jan 2013 Procure multiple experimental runs but limited data interpretation. Effort focused on methodology and execution

Jan – Aug 2013 Testing suspended due to installation challenges and other NaTeF testing obligations (Swift)

Aug 2013 Resume project, review of literature on the method as well as Dr. John Graham's work

28 Aug 2013 Clean equipment, recalibrate, and restart effort using information from previous effort, the literature review and supplier technical assistance.

28 Aug 2013 TGA gas controller stops

28 Aug – 7 Oct 2013 Interpretation of previously procured data

17 Sept 2013 TGA gas controller repaired

Aug – Sept 2013 Begin collecting simulated distillation information on soaking fluids

Experimental

Materials

A sample set of four polymers were received from two manufactures was procured. The sample set was comprised of EPDM, fluorocarbon, fluorsilicone and nitrile. Samples were procured from Trelleborg and from Simrit seals. These four materials covered the greatest majority of seal materials found in aerospace systems.

Three different test fluids were used for the exposure.

1. Aromatic 150, a controlled aromatic blend used for aromatic studies. Comprised of heavy petroleum aromatics, the blend is controlled to provide a 150 °C flashpoint. A typical blend is 10-20% 1,2-dimethyl-4-ethylbenzene, 10-20% 1,2,3,5-tetramethylbenzene and the remainder various enantiomers of tetramethylbenzene and dimethyl ethylbenzene.
2. Jet fuel as a locally procured Jet A from a previous research project.
3. S-8, Sasol synthetic jet fuel provided by WPAFB and being used in a concurrent research project.

The inert environment is provided using K-bottles of analytical grade nitrogen.

The TGA instrument being used is a TA Instruments Q50. The instrument is designed to work with the Thermo-Nicolet products in a nearly plug and play manner. The best feature of the Q50 with respect to this research is the accurate and reliable vertical thermobalance housed in a temperature-compensated environment. It uses an industry-standard null-balance principle, which is free from the baseline complications. The balance provides the best accuracy and precision in weight change detection from ambient to 1000°C, low baseline drift, and sensitive, reliable operation over the entire weight range of the instrument. The system is equipped with an EVA furnace that connects to the heated transfer lines.

The FT-IR being used is the Thermo-Nicolet 6700. Besides the ability to connect the FTIR easily to the TA Instruments TGA, the Nicolet 6700 has dynamic alignment to facilitate good signal to noise ratios, which can be a problem with gas phase analyses. For these experiments the entire spectral range of 4000 to 400 cm^{-1} was collected.

Method

In order to explore the best testing parameters for this research, testing has been done using a number of thermal environments. Ramp rates of 5°C and 10°C/min have been used. Incorporation of isothermal holds was used to evaluate the benefits of letting the system “catch-up”. An attempt at using a negative temperature ramp was also made. While the temperature did drop, there did not appear to be probative data obtained from the cooling period. Using both an inert environment for the entire run and the use of an oxidizing environment were evaluated. A gas change was made at 600°C with the result of almost instantaneous oxidation of the sample and the evolution of CO, CO₂ and H₂O. Runs were made to 600°C, 800°C and 900°C.

The current TGA program being used is a 5°C/min ramp from room temperature to 900°C in an inert environment (N₂). The average sample size is 5 to 12mg. The infrared resolution is 8, with a sample interval of 10 seconds. The reconstructions of total IR response vs. time (Gram-Schmidt reconstruction) is collected and used to identify times of maximum infrared response. The interferograms for every individual scan are also saved. The heated transfer line is maintained at 200°C and the heated gas cell within the FT-IR is maintained at 210°C. This temperature differential helps assure that if the evolved gases condense within the system, it occurs in the easier to clean sample line as opposed to the FT-IR cell.

The current experimental method is to allow the instruments to equilibrate to temperature. This also helps assure the FT-IR cell is dry and free from atmospheric CO₂ and H₂O. Because any changes to the thermal environment change the FT-IR response, a background is collected for every sample run. The background and series vectors are collected while the TGA is cycling through a tare process. During the tare process, the furnace is closed and it is believed this may help further purge the system of atmospheric CO₂ and H₂O.

Once the sample pan has been tared, a small piece of sample is placed on the platinum sample pan. The goal is to have a sufficiently large sample to provide enough vapors for the FT-IR to see without having so much that it causes fluctuations in the TGA weight loss curve. Sample sizes of 7-12mg have been used successfully.

The current program runs for 181 minutes on the TGA. The FT-IR is configured to collect spectra for 190 minutes.

After completion of the run, the TGA data is exported into a file that can be imported into the Nicolet Ominic software for comparison to the Gram-Schmidt reconstruction. Ideally the two graphs should be visually similar.

After the run, the data is prepared as a thermogravimetric chart with weight loss, weight loss with respect to time and with respect to temperature. An analysis of weight change provides information on how much weight has been lost in each reaction (Figure 1). By comparing the time at which the maximum rate of change in weight loss occurs to the Gram-Schmidt maximum at a similar time, it is possible to identify the corresponding infrared spectrum to the gas evolution (Figure 2 and Figure 3).

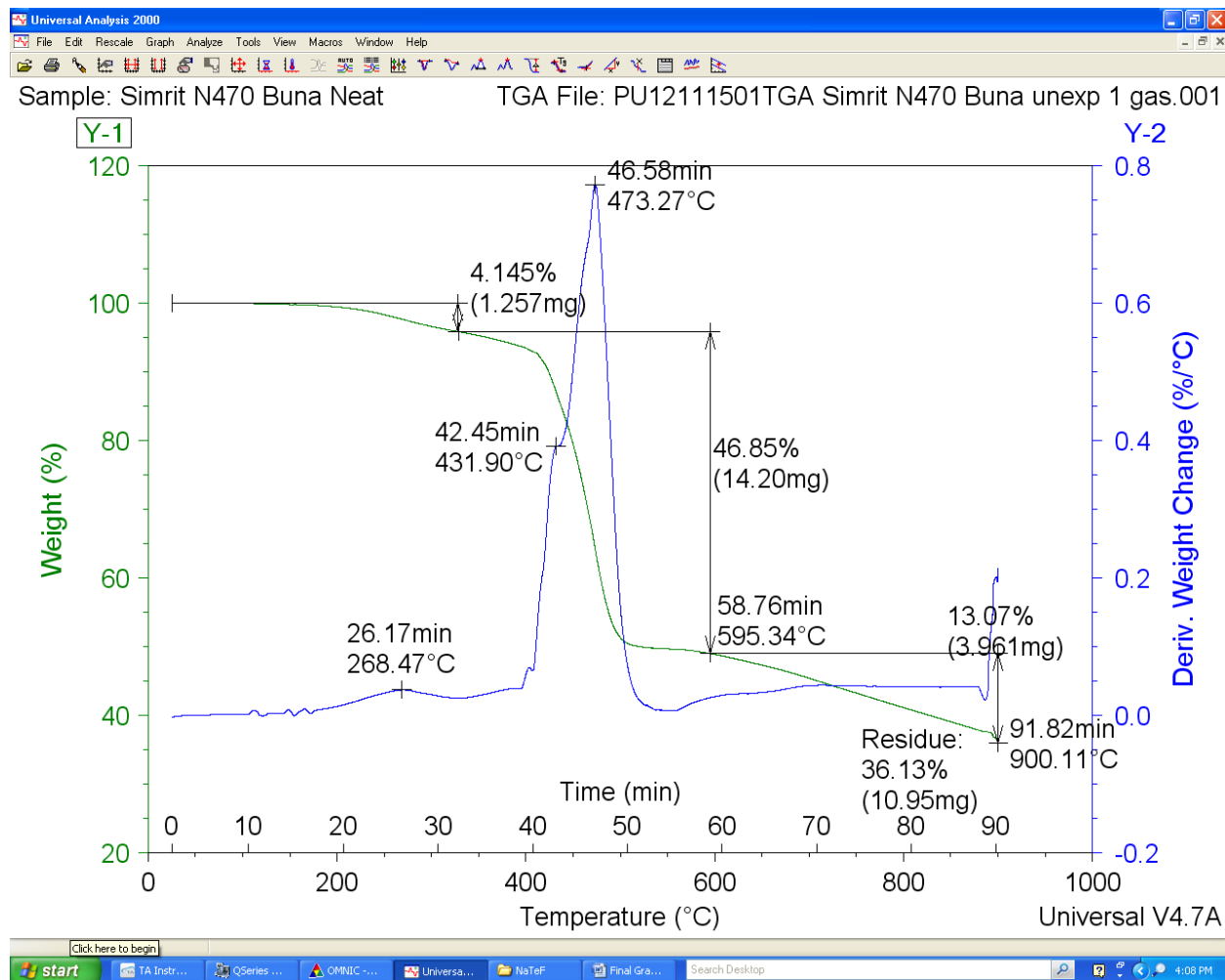


FIGURE 1 - REPRESENTATIVE TGA ANALYSIS

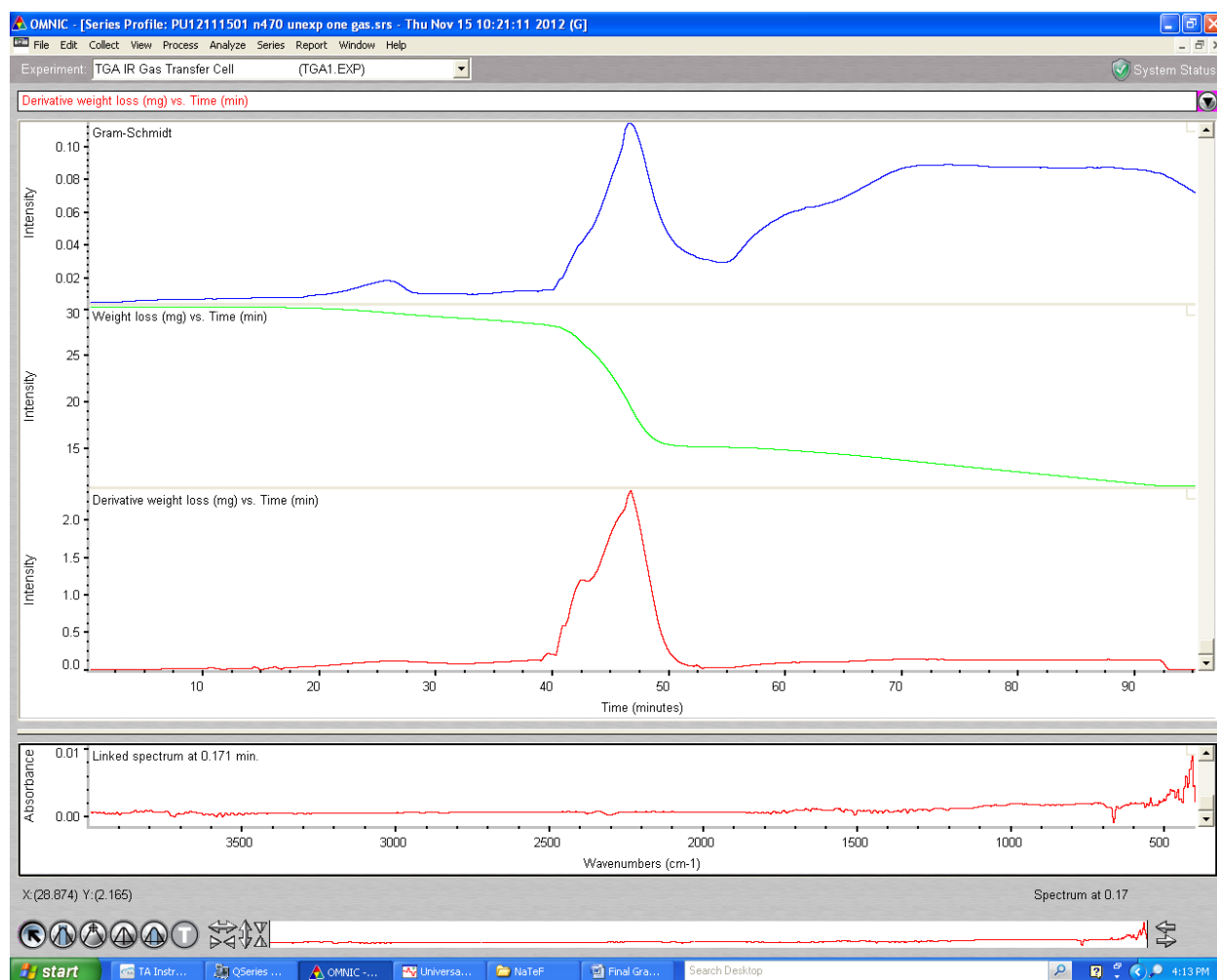


FIGURE 2 - REPRESENTATIVE GRAM-SCHMIDT AND CORRESPONDING TGA SCANS

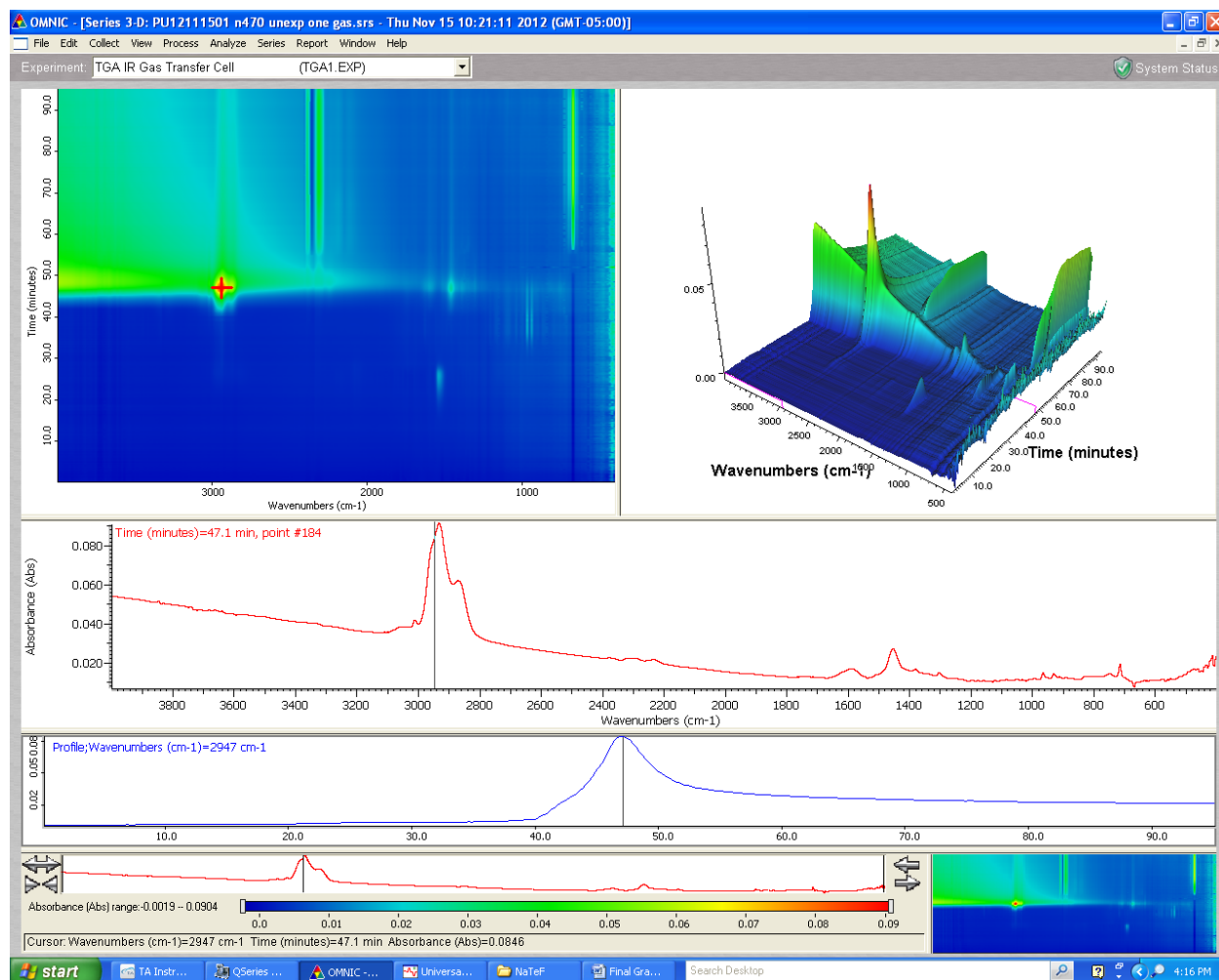


FIGURE 3 - REPRESENTATIVE SERIES DISPLAY OF CORRESPONDING FT-IR DATA

Current Results

Execution of test method

It was concluded that the use of an oxidizing environment (dry air) during the TGA experiment was not value added. The only purpose to the oxidizing environment would be to separate inert fillers from reactive ones. For this experiment there does not appear to be value in this analysis. The absolute amount of non-reactive fillers will not change and the relative amount will be captured as a result of the % weight change analysis. There is no FT-IR information to be gained as the resultant gases are primarily CO, CO₂, and water. Any change to the polymer structure should be seen as a result of a change to reactions taking place in the inert atmosphere.

The primary tool available for increasing the amount of information collected will be the heating rate. By slowing the rate, there should be an increase in separation between reactions and the components evolving at different temperatures. This may prove unnecessary if there are no reactions taking place close to each other.

Based on the data and the literature reviews, there may not be a value in an isothermic hold. As long as the ramp rate is slow enough for the thermal reactions to take place matched to the

environment, any change in the polymer system it should show up in the TGA scan. The only other consideration is sufficient time for the evolved gases to pass to the FTIR through the heated transfer lines. Results to date indicate the time lag is relatively short (60 -90 seconds), however in some cases the resultant waterfall display of the FT-IR data suggests holdup of gases. This is most often observed in the presence of oxidation gases.

It is also important to consider dehydration, i.e. actually “drying” the sample. This removal of water may be from the surface or out of the part. It may also be an actual dehydration reaction where an OH radical and an H radical are removed from the sample and the radicals combine to form water. Any water evolved will be spectrally active in the FT-IR analysis.

For interpreting the TGA spectra, the most important point is the inflection point. This is the point where there is the greatest rate of change with respect to the weight change. By taking this time and temperature, it is possible to locate in the FTIR data the spectrum that most closely corresponds to this point in the TGA. The point of greatest weight change is most likely to have the greatest concentration of gas for that particular weight loss. This inflection point is identified by the first derivative of the weight loss curve.

It was also learned that the use of a water trap to collect the evolved vapors created too much of a back pressure on the system, preventing the vapors from moving from the EVA furnace on the TGA through the heated transfer lines and into the FT-IR heated gas cell. The use of the water trap was eliminated.

Simulated Distillation

In order to determine the temperature(s) at which the various test fluids are volatilized by the TGA, a simulated distillation test was performed. From this experiment it was possible to determine the test fluid Aromatic 150 began to show weight loss at room temperature (25°C) and was done by 130°C. JP8 weight loss began at 65°C and was done by 165°C and S-8 synthetic fuel weight loss began at 37°C and was done by 155°C.

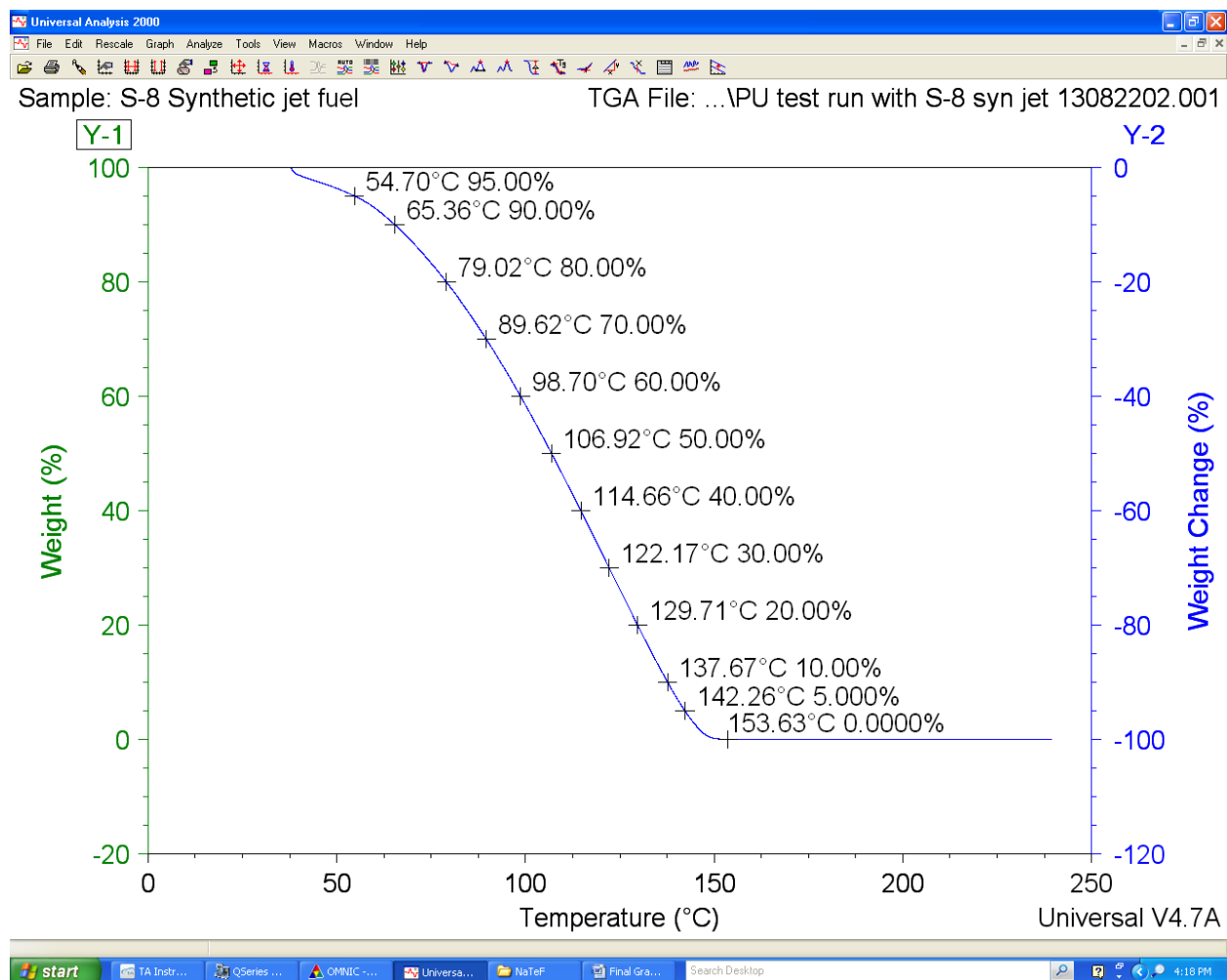


FIGURE 4 - EXAMPLE SIMULATED DISTILLATION

Research Findings

Analysis of the collected data continues. However to date it has been determined that it is possible to connect the evolution of gas as indicated by the inflection point on the TGA scan to a maximum on the Gram-Schmidt reconstruction within 1 to 2 minutes.

The exposed samples run to date have not all been analyzed but none of the scans that have been analyzed show measureable weight loss in the region attributed to the test fluids. This suggests that any interaction with the test fluid is either not a simple “soaking in” of the fluid or it is insufficient to be seen by the method.

To date the analyses of nitrile and EPDM materials have not shown significant differences between exposed and unexposed samples. The time and temperature of the inflection points are relatively constant and the % weight losses are similar. There is some variation and further testing is necessary to determine if this is due to natural variations or due to actual interactions between the polymers and the test fluids.

Next Steps/Continuation Plans

- Further analyses of the weight loss ratios, times, and temperatures must be made. The TGA is capable of high repeatability between runs of standards, so the observed variations may be real.
- Perform more in-depth analyses of the TGA spectra and the corresponding FT-IR spectra to determine if the evolution of the test fluids is present. Analyses to date have been inconclusive to negative.
- Continue to generate data to develop a sense of precision and accuracy between sample runs.
- Repeat the experiment on samples exposed to test fluids known to result in material attack to provide information regarding what an attacked rubber looks like on the TGA and FT-IR as compared to unexposed material.
- Run contact attenuated total reflection on exposed and unexposed samples to provide FT-IR spectral information separate from thermal degradation.
- Run FT-IR analysis on standard pyrolysis samples of the exposed and unexposed samples for comparison to the resultant evolved gases.

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